APPLICATIONS OF POLYOXOMETALATES AND THEIR DERIVATIVES

Synopsis of the thesis submitted to Madurai Kamaraj University, Madurai in partial fulfilment of the requirements for the award of the degree of

Doctor of Philosophy in Chemistry

by

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Introduction

Polyoxometalates (POMs) are early transition metal-oxygen anion clusters. More specifically, they are oligomeric aggregates of metal cations bridged by oxide anions and formed by self-assembly processes. In recent years POMs and their modified derivatives become attractive catalysts towards several organic transformations both in homogeneous and heterogeneous reaction conditions. Due to their redox characteristics they act as flexible catalysts for a variety of transformations such as electron-transfer reactions carried out by chemical, electro-chemical and photochemical means. The reasons for the attraction towards the use of HPOMs as catalyst are as follows:

- HPOMs are highly efficient;
- HPOMs are resistant to oxidative degradation and hydrolysis;
- HPOMs can stabilize metal ions that are unstable in air;
- HPOMs are environmentally benign.

However, owing to their small surface area (<10 m^2 g^{-1}) and separation problems from the reaction mixture, their catalytic performances are often limited to heterogeneous catalysis. For that reason, in general the POMs are supported on organized media such as clay minerals and thereby increase the surface area and to make the active sites of POM more accessible to reactants. In particular, acid treated clay catalysts have established large attention in synthesis of different organic derivatives, as catalysts or as supports, because of their environmental friendly, low cost and cleanness of uses.

For the past two decades we have been working in the field of POMs. Previously we focused on the structural diversity, spectral and electro-chemical characterization of the mixed-valence heteropolyoxometalates and the study of electron-transfer ability of POM towards variety of organic transformations. Recently we reported the catalytic ability of the POM supported natural clay materials in the synthesis of variety of organic compounds. In continuation of our effort this work is an attempt to investigate new green synthetic protocols for the synthesis of some biologically interesting N-containing heterocyclic compounds using heteropolyoxometalate supported montmorillonite K-10 clay materials as catalyst. The thesis consists of eight chapters and the contents are summarized as follows.

Chapter 1

This chapter discusses about the introductory aspects of heteropoly acids (HPAs), clay minerals especially about montmorillonite K-10 and the role of HPAs supported on clay materials towards the multi-component reactions in organic synthesis. The aims and objectives of the present work are also given.

Chapter 2

Materials used for the present study and the general physical and analytical methods followed are discussed in this chapter. Preparation and purification of the following heteropoly acids (HPAs) used for the preparation of catalytic materials used in the present study are also discussed in this chapter.

1. $H_3[PMo_{12}O_{40}]$, (PMo)
2. $H_4[PVMo_{11}O_{40}]$, (PVMo)
3. $H_5[PV_2Mo_{10}O_{40}]$, (PV_2Mo) and HPA supported on Mont K-10 such as
4. 10% $H_3[PMo_{12}O_{40}]$ over Mont K-10, (10% PMoK-10)
5. 5% $H_4[PVMo_{11}O_{40}]$ over Mont K-10, (5% PVMoK-10)
6. 10% $H_4[PVMo_{11}O_{40}]$ over Mont K-10, (10% PVMoK-10)
7. 20% $H_4[PVMo_{11}O_{40}]$ over Mont K-10, (20% PVMoK-10)
8. 30% $H_4[PVMo_{11}O_{40}]$ over Mont K-10, (30% PVMoK-10) and
9. 10% $H_5[PV_2Mo_{10}O_{40}]$ over Mont K-10, (10% PV_2MoK-10).

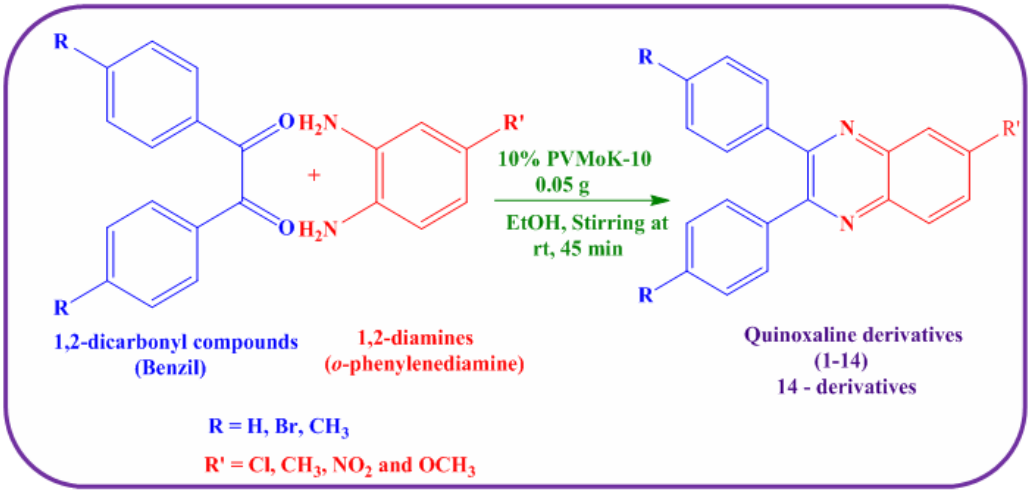
Chapter 3

The FT-IR spectral characterization of the HPAs; PMo, PVMo and PV_2Mo used for the preparation of catalytic materials used in the present study are discussed in this chapter. The catalytic material HPA, $H_4[PVMo_{11}O_{40}]$ supported montmorillonite K-10 clay (PVMoK-10) has been thoroughly characterized by FT-IR, XRD, HR-SEM and EDX methods. Further the sustainability of the catalytic materials has also been evolved through XRD and SEM measurements.

Chapter 4

This chapter deals with the synthesis of the quinoxaline derivatives through the one-pot two-component condensation reaction of variety of substituted aromatic 1,2-dicarbonyl compounds and aromatic substituted 1,2-diamino compounds catalyzed by heteropoly-11-molybdo-1-vanadophosphoric acid, $H_4[PVMo_{11}O_{40}]$ supported on Mont K-10 clay (PVMoK-

10) in ethanol solvent medium under the condition of stirring at room temperature. The general reaction pattern is given in Scheme 1.



Scheme 1 Synthesis of quinoxaline derivatives catalysed by 10% PVMoK-10

In this manner the following fourteen quinoxaline derivatives (**1 -14**) are synthesized and the compounds are identified with the aid of melting point measurements and elemental analysis. Further the compounds are characterized with the aid of FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic methods.

1. 2,3-diphenylquinoxaline

2. 6-chloro-2,3-diphenylquinoxaline

3. 6-methyl-2,3-diphenylquinoxaline

4. 6-methoxy-2,3-diphenylquinoxaline

5. 6-nitro-2,3-diphenylquinoxaline

6. 2, 3-bis(4-methylphenyl)quinoxaline

7. 2, 3-bis(4-methylphenyl)6-chloroquinoxaline

8. 2, 3-bis(4-methylphenyl)6-methylquinoxaline

9. 2, 3-bis(4-methylphenyl)6-methoxyquinoxaline

10. 2, 3-bis(4-methylphenyl)6-nitroquinoxaline

11. 2, 3-bis(4-bromophenyl)quinoxaline

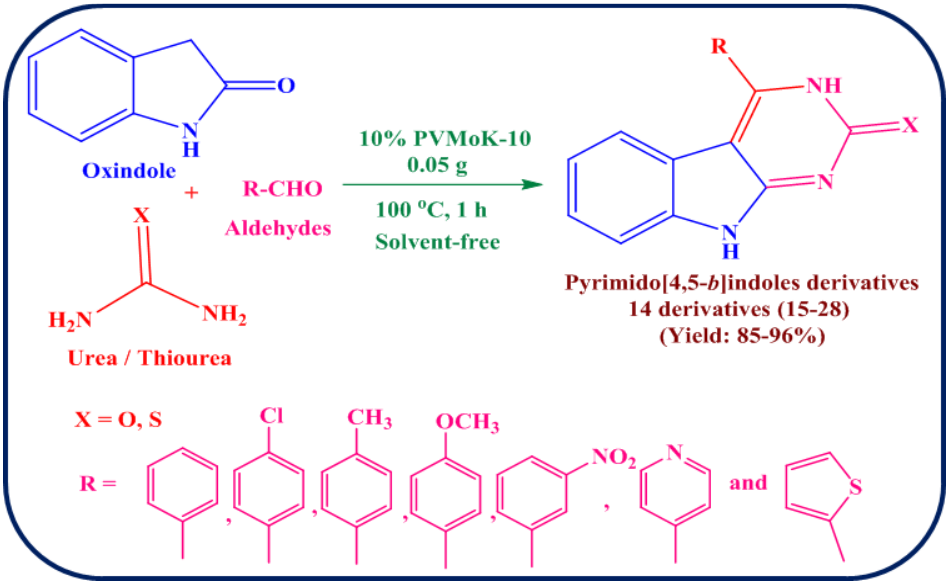
12. 2, 3-bis(4-bromophenyl)6-chloroquinoxaline

13. 2, 3-bis(4-bromophenyl)6-methylquinoxaline

14. 2, 3-bis(4-bromophenyl)6-nitroquinoxaline

Chapter 5

This chapter deals with the synthesis of the pyrimido[4,5-b]indole derivatives through the one-pot three-component condensation reaction of oxindole, variety of substituted aromatic aldehydes and urea / thiourea catalyzed by heteropoly-11-molybdo-1-vanadophosphoric acid, $H_4[PVMo_{11}O_{40}]$ supported on Mont K-10 clay (PVMoK-10) under solvent free green reaction condition. The general reaction pattern is given in Scheme 2.



Scheme 2 Synthesis of pyrimido[4,5-*b*]indoles catalysed by 10% PVMoK-10

In this manner the following fourteen pyrimido[4,5-b]indole derivatives **(15-28)** are synthesized and the compounds are identified with the aid of melting point measurements and elemental analysis. Further the compounds are characterized with the aid of FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic methods.

15. 4-phenyl-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-one

16. 4-(4-chlorophenyl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-one

17. 4-(p-tolyl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-one

18. 4-(4-methoxyphenyl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-one

19. 4-(3-nitrophenyl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-one

20. 4-(4-pyridine-4-yl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-one

21. 4-(thiophene-2-yl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-one

22. 4-phenyl-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-thione

23. 4-(4-chlorophenyl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-thione

24. 4-(p-tolyl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-thione

25. 4-(4-methoxyphenyl)- 3,9-dihydro-2H-pyrimido[4,5-b]indole-2-thione

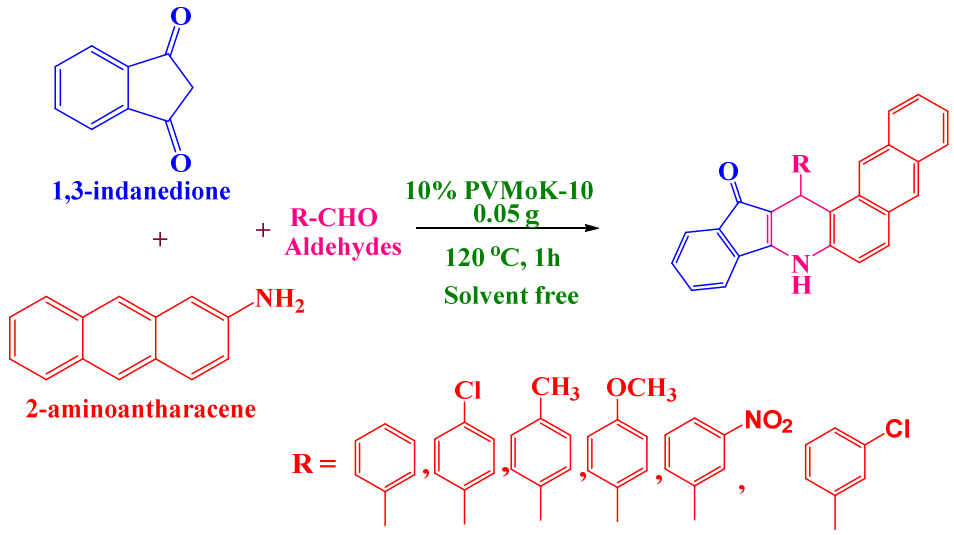
26. 4-(3-nitrophenyl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-thione

27. 4-(4-pyridine-4-yl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-thione

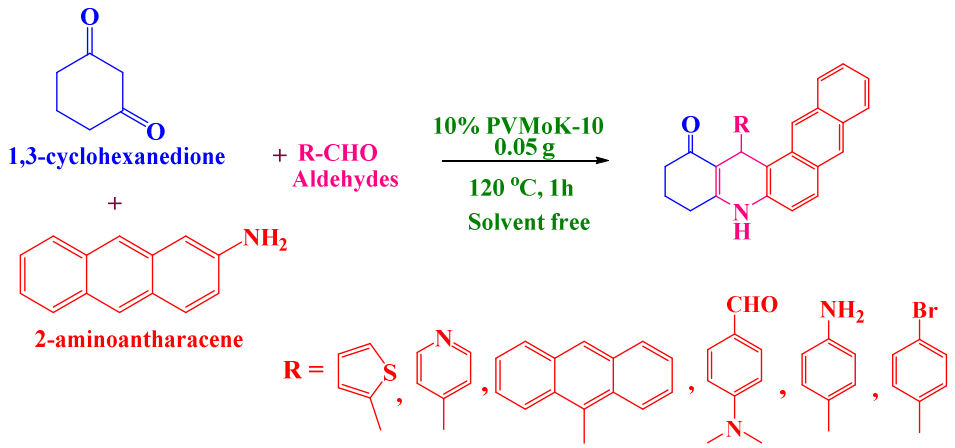
28. 4-(thiophene-2-yl)-3,9-dihydro-2H-pyrimido[4,5-b]indole-2-thione

Chapter 6

This chapter deals with the synthesis of the naphtho[2,3-f]quinolin-13-one and naphtho[2,3-a]acridin-1(2H)-one derivatives through the one-pot three-component condensation reaction of 2-aminoanthracene, variety of substituted aromatic aldehydes and 1,3-indanedione / 1.3-cyclohexanedione catalyzed by heteropoly-11-molybdo-1-vanadophosphoric acid, $H_4[PVMo_{11}O_{40}]$ supported on Mont K-10 clay (PVMoK-10) under solvent free green reaction condition. The general reaction pattern is given in Scheme 3 & 4.



Scheme 3 Synthesis of naphtho[2,3-f]quinolin-13-one derivatives using 10% PVMoK-10 as a catalyst



Scheme 4 Synthesis of naphtho[2,3-a]acridin-1(2H)-one derivatives using 10% PVMoK-10 as a catalyst

In this manner the following six naphtho[2,3-f]quinolin-13-one derivatives (**29 – 34**) and six naphtho[2,3-a]acridin-1(2H)-one derivatives **(35 - 40)** are synthesized and the compounds are identified with the aid of melting point measurements and elemental analysis. Further the compounds are characterized with the aid of FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic methods.

29. 14-phenyl-8,14-dihydro-13H-indeno[1,2-b]naphtho[2,3-f]quinolin-13-one

30. 14-(4-chlorophenyl)-8,14-dihydro-13H-indeno[1,2-b]naphtho[2,3-f]quinolin-13-one

31. 14-(p-tolyl)-8,14-dihydro-13H-indeno[1,2-b]naphtho[2,3-f]quinolin-13-one

32. 14-(4-methoxyphenyl)-8,14-dihydro-13H-indeno[1,2-b]naphtho[2,3-f]quinolin-13-one

33. 14-(3-nitrophenyl)-8,14-dihydro-13H-indeno[1,2-b]naphtho[2,3-f]quinolin-13-one

34. 14-(3-chlorophenyl)-8,14-dihydro-13H-indeno[1,2-b]naphtho[2,3-f]quinolin-13-one

35. 14-(thiophen-2-yl)-3,4,5,14-tetrahydronaphtho[2,3-a]acridin-1(2H)-one

36. 14-(pyridin-4-yl)-3,4,5,14-tetrahydronaphtho[2,3-a]acridin-1(2H)-one

37. 14-(anthracen-1-yl)-3,4,5,14-tetrahydronaphtho[2,3-a]acridin-1(2H)-one

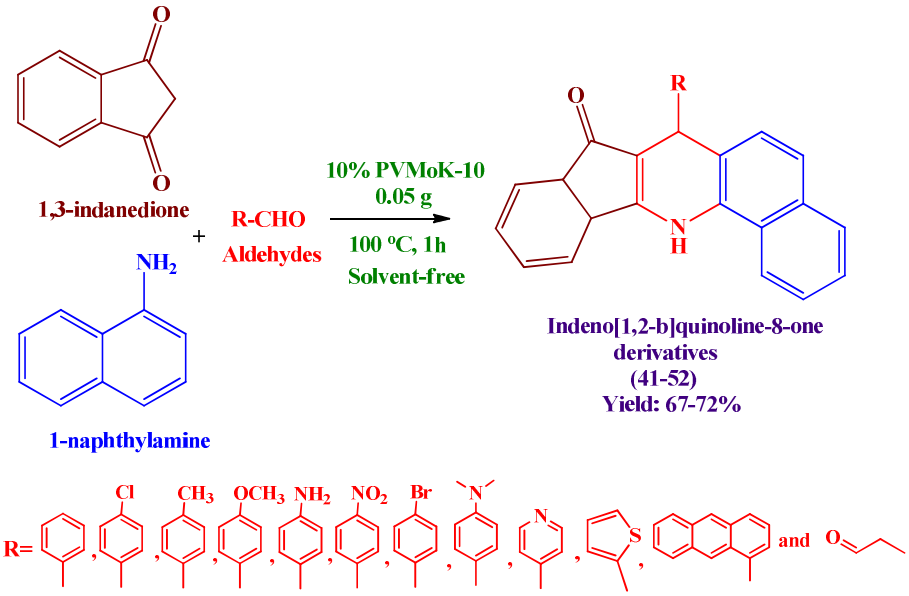
38. 14-(4-(dimethylamino)phenyl)-3,4,5,14-tetrahydronaphtho[2,3-a]acridin-1(2H)-one

39. 14-(4-bromophenyl)-3,4,5,14-tetrahydronaphtho[2,3-a]acridin-1(2H)-one

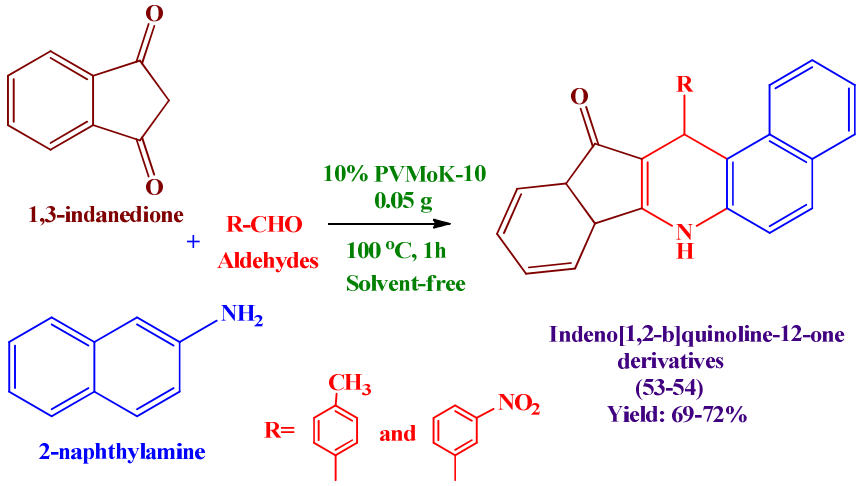
40. 14-(4-aminophenyl)-3,4,5,14-tetrahydronaphtho[2,3-a]acridin-1(2H)-one

Chapter 7

This chapter deals with the synthesis of the indeno[1,2-b]quinoline-8-one and indeno[1,2-b]quinoline-12-one derivatives through the one-pot three-component condensation reaction of 1,3-indanedione, variety of substituted aromatic aldehydes and 1-naphthylamine / 2-naphthylamine catalyzed by heteropoly-11-molybdo-1-vanadophosphoric acid, $H_4[PVMo_{11}O_{40}]$ supported on Mont K-10 clay (PVMoK-10) under solvent free green reaction condition. The general reaction pattern is given in Scheme 5 & 6.



Scheme 5 Synthesis of indeno[1,2-*b*]quinoline-8-one derivatives using 10% PVMoK-10 catalyst.



Scheme 6 Synthesis of indeno[1,2-*b*]quinoline-12-one derivatives using 10% PVMoK-10 catalyst.

In this manner the following twelve indeno[1,2-b]quinoline-8-one derivatives (**40 -52**) and two indeno[1,2-b]quinoline-12-one derivatives (**53 & 54**) are synthesized and the compounds are identified with the aid of melting point measurements and elemental analysis. Further the compounds are characterized with the aid of FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic methods.

41. 7-Phenyl-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

42. 7-(4-Chlorophenyl)-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

43. 7-(4-Methylphenyl)-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

44. 7-(4-Methoxyphenyl)-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

45. 7-(4-Aminophenyl)-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

46. 7-(4-Nitrophenyl)-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

47. 7-(4-Bromophenyl)-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

48. 7-(4-Dimethylamino)phenyl)-7,13-dihydro-8H-benzo[h]indeno[1,2-b] quinolin-8-one

49. 7-(Pyridin-4-yl)-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

50. 7-(Thiophen-2-yl)-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

51. 7-(Anthracen-1-yl)-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

52. 7-Ethyl-7,13-dihydro-8H-benzo[h]indeno[1,2-b]quinolin-8-one

53. 13-(p-tolyl)-7,13-dihydro-12H-benzo[f]indeno[1,2-b]quinolin-12-one

54. 13-(3-nitrophenyl)-7,13-dihydro-12H-benzo[f]indeno[1,2-b]quinolin-12-one

Chapter 8 Summary

This chapter summarizes the results of the investigations. In this work HPA supported on Mont K-10 clay based four different green routes for the synthesis of 54 different organic compounds have been proposed. Further the HPA based catalysts were found to be reused several times without significant loss of their catalytic activity. Green heterogeneous reaction condition, simple workup procedure, short reaction time, high yield of products and reusability of the catalyst are the added advantages of the present investigations.

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Notification of online Ph.D. Public Viva-Voce Examination

As per the regulations of the Madurai Kamaraj University, Madurai, I am very happy to inform you that the Ph.D., Public *viva-voce* examination of my Scholar Mr. M.Kumaresan, who has submitted his Ph.D., thesis to Madurai Kamaraj University will be conducted through online mode *via* Google Meet as per the details given below.

Candidate	:	**Mr. M. KUMARESAN, M.Sc., (Regn No:F9625)** Formerly Research Scholar, Department of Chemistry, VHNSN College (Autonomous), Virudhunagar
Title of the Ph.D. Thesis	:	"**APPLICATIONS OF POLYOXOMETALATES AND THEIR DERIVATIVES**"
Date & Time	:	**11th November 2020 at 11.00 a.m**
Venue	:	**Department of Chemistry,** V.H.N.S.N. College (Autonomous), Virudhunagar
Supervisor &Convener of Viva-voce Board	:	**Dr.P.SAMI, M.Sc., M.Phil., Ph.D.,** Associate Professor of Chemistry, V.H.N.S.N. College (Autonomous), Virudhunagar
External Examiner	:	**Dr. Chinnakonda S. Gopinath, FASc,** Senior Principal Scientist, (Scientist F) Catalysis Division & Centre of Excellence on Surface Science, CSIR – National Chemical Laboratory, Dr. Homi Bhabha Road, Pune – 411 008.

To join click this link via Google meet: https://meet.google.com/eow-rduf-cxq

The Synopsis of the thesis is available in the College Website and a copy of the thesis is available in the Department Library, Department of Chemistry, V.H.N.S.N. College (Autonomous), Virudhunagar for your reference.

All are Cordially Invited

Supervisor & Convener of
Viva-voce Board.

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